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Abstract

In an effort to texture a glass surface with alumina particles, we found that positively charged alumina particles were only attracted to the negatively charged silica substrates in aqueous solution for a very short period although the pH was between the iso-electric-point (IEP) of alumina and silica. Instead, experiments show that the glass surface attracted the dissolved species of alumina, which made the surface repel the alumina particles. It was observed that the IEP of the glass, which was exposed to the supernatant of centrifuged alumina particles, shifted toward the IEP of alumina: the magnitude of the shift depended on the concentration of the dissolved alumina, and vice versa for the IEP of the alumina exposed to a supernatant formed with glass powder. Therefore after a short exposure to an alumina slurry, the glass surface 'look' look like alumina, and the electrostatic attraction between glass and alumina particles will no longer exist.

1. Introduction

Ceramic surfaces generally acquire a surface charge when exposed to water. The surface is composed of neutral -MOH sites that react with H^+ and OH^- ions to produce either positive (-M^+) or negative (-O^-) surface sites, respectively, and water molecules. The reaction of H^+ and OH^- with the neutral sites is competitive; at lower pH, the H^+ reaction dominates and the surface is composed of more positive sites than negative sites, whereas at higher pH, the OH^- reaction dominates and the surface is composed of more negative sites. At a specific pH, known as the isoelectric point (IEP), the surface is neutral, composed of equal fractions of positive and negative sites. Since the IEP depends on the chemistry of the surface, at a given pH, the surface of one material can have a net negative charge, whereas a second surface, composed of a different material, can have a net positive charge. For this condition, the pH used to produce these observations is between the IEP of the two materials.

Studies¹⁻⁵ of slurries consisting of two different powders, where particles of one powder have a different IEP relative to the second, have produced two interesting observations when the slurry is formulated at a pH between the IEPs of the two. The first phenomenon occurs when the particles of the two powders are approximately of the same size; in this case, particles of the two powders, one being positive, the other negative, attract one another to form a strongly attractive particle network composed of the two powders. The second observation occurs when one set of particles is much smaller than the other. In this case, the smaller particles are attracted and stick to the surface of the much larger particles. As more and more small particles cover and form a monolayer on the larger particles, the apparent surface charge of the larger particles appears to change its sign to that of the smaller particles. Once a monolayer is fully formed, the larger particles now repel the smaller particles due to phenomena used to describe the DLVO theory.

As detailed elsewhere⁵, the phenomena where particles could be used to texture a flat surface appeared to be an attractive method to produce a super-hydrophobic surface, which requires a 'hill and valley' surface topography that can be functionalized with hydrophobic molecules. Though trial and error, flat alumina surfaces could be textured with small silica particles at a pH between their IEPs, and likewise, flat glass surfaces could be texture with small alumina particles, it became evident that the simple explanation described above for their mutual attraction was not observed. Instead it was observed by one of our co-authors that when the flat surface was exposed to a dilute slurry, particles would be attracted to the surface for only a short period, then repelled despite the fact that few particles covered the surface. This observation suggested that something was poisoning the surface after it was exposed to the dilute slurry. Several experiments quickly showed that the aqueous slurries not only contained charged particles, but also contained soluble species that appear to have the same charge as the particles themselves. Here we describe the results of experiments that confirm this observation, and show that the soluble species specifically adsorb on the surface and change the IEP of the surface to that of the soluble species.

2. Experiments

Two series of experiments were performed. In one series, aqueous slurries were formulated with two different alumina powders at pH 3.5; in the second series, slurry was formed with glass powders at the same pH. pH 3.5 is between the IEPs of both powders (IEP of alumina: pH 9, IEP of glass: pH 2). In the first series, the alumina slurries were aged for 2 days to mimic the procedure used to coat glass slide with alumina particles. In the second series, glass slurries were aged for 4 weeks to let the concentration of the dissolved silica reach equilibrium⁶.

The slurries were centrifuged (Marathon 1200, Fisher Scientific) at 1500 rpm for 20 minutes to separate all particles to form a clear supernatant containing soluble species resulting from ageing. The concentration of dissolved alumina in the first series of supernatants was changed by using two alumina powders with very different specific surface areas, while the concentration of dissolved glass in the second series supernatant was changed by mixing the saturated supernatant with different amounts of deionized water. Each of the two supernatants were then mixed with the other kind of powder, namely, the supernatant from the silica slurry was mixed with alumina powder, and vice versa, in a ratio of one liter of supernatant to 50mg of powder. Succeeding zeta potential measurements were performed on these mixtures as a function of pH. Two different alumina powders, namely one with a particle size of 0.7 μm (AA-07, Sumitomo Corp., Japan) and another with a particle size of 5 μm (AA-5, Sumitomo Corp., Japan), were used. The glass powder was obtained by grinding glass slides (Microscope Cover Glass 12-540-A, Fisher Scientific), and has an average size of 1.26 μm .

3. Results and Discussion

Figure 1 reports the Zeta potential vs. pH for the glass powder in water and in supernatants of 0.7 μm and 5 μm Al_2O_3 powders. The figure shows that the IEP for the glass powders shifts from approximately pH 2 for DI water, to pH 5.5 for the supernatant formed with the alumina

powders of the larger particles size, and to pH 7 for the supernatant formed with the alumina powders of the much smaller particle size. Figure 2 reports the zeta potential vs pH for slurries formulated with the 0.7 μ m alumina powder in mixtures of supernatant of glass and deionized water. The IEP of the alumina powders in DI water is at pH 9, as expected, and systematically drops to pH 6 when introduced into supernatants containing increasing silica content.

In both series, it can be postulated that the change in the IEP is due to soluble ionic species within the supernatants. It is possible to have soluble species that include Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$ and $\text{Al}(\text{OH})_4^-$, but at the pH 3.5, where the current work was conducted, literature ⁷ suggests that the dominate species is Al^{3+} . This specific species would bond with a negative site on the silica surface to not only compensate but also reverse charge to positive. Thus, since the adsorption of the charged alumina species decreases the number of negative surfaces sites and increases the number of positive surface sites per unit area, the IEP of the silica powder will shift to higher values of pH. Concurrent with this shift in IEP, the chemistry of the silica surface changes to that of an alumina surface; namely, the silica surface becomes coated with alumina. Although not observed in the current experiments, the IEP of the silica surface would be expected to shift to pH 9 when the silica surfaces are fully covered with alumina species similar to that reported for silica particles in aqueous AlCl_3 solutions ⁸. In the current experiments, it appears that the concentration of dissolved alumina species produced after several days of aging depends on the size of the alumina particles. Namely, smaller alumina particles with a larger surface area per unit volume appear to produce a greater concentration of soluble alumina species for a given aging period. It is interesting to note that Iler ⁹ found that the adsorption of alumina onto the surface of colloidal silica particles greatly reduced the solubility of silica in water.

Likewise, Figure 2 shows that the soluble silica species within the supernatants of the silica slurries are attracted to the positive surface sites on the alumina particles. The solubility of silica at room temperature in water is about 120ppm ⁶. The dissolved silica is mostly monosilicic acid $\text{Si}(\text{OH})_4$ ^{6,10}. It is a weak acid, of which the first degree disassociation produces H_3SiO_4^- and H^+ at a pH less than 9, and at higher pH, $\text{Si}(\text{OH})_4$ further disassociates into $\text{H}_2\text{SiO}_4^{2-}$ / HSiO_4^{3-} / SiO_4^{4-} and produces more H^+ ¹¹.

For a pH less than 9 (approximate IEP for alumina), the surface of Al_2O_3 particles is positively charged, and the negatively charged HSiO_4^- is attracted and neutralizes the local charge. Because the elimination of the positive surface sites the IEP of Al_2O_3 shifts to lower pH. As H_3SiO_4^- is depleted from the solution by adsorption, its disassociation is driven forward to maintain an equilibrium concentration. The SiO_2 ‘coating’ on the Al_2O_3 particles is determined by the concentration of dissolved $\text{Si}(\text{OH})_4$. As shown in Figure 2, as the concentration of the silica supernatant increases, the IEP of Al_2O_3 is driven towards lower pH.

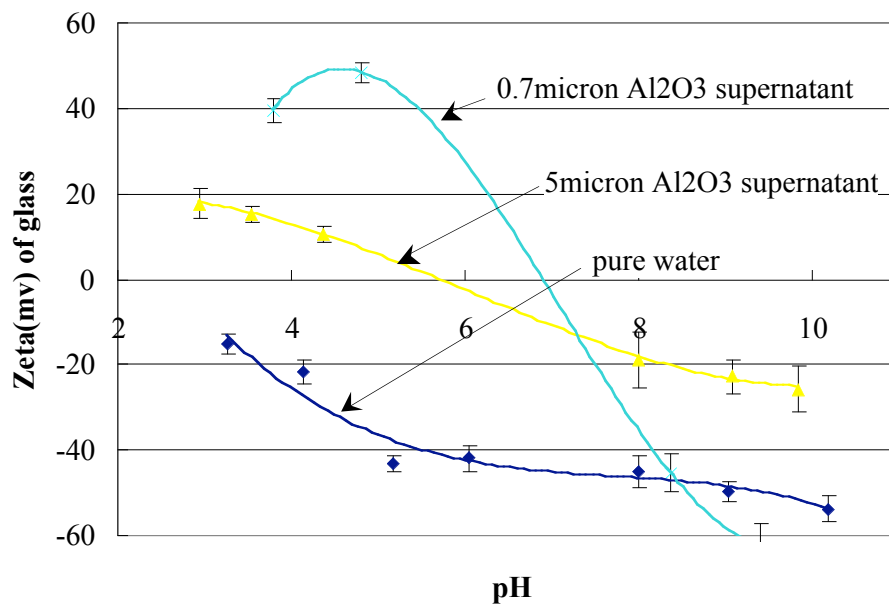


Figure 1 Zeta potential of glass powder in water and supernatant of 0.7 μm and 5 μm Al_2O_3

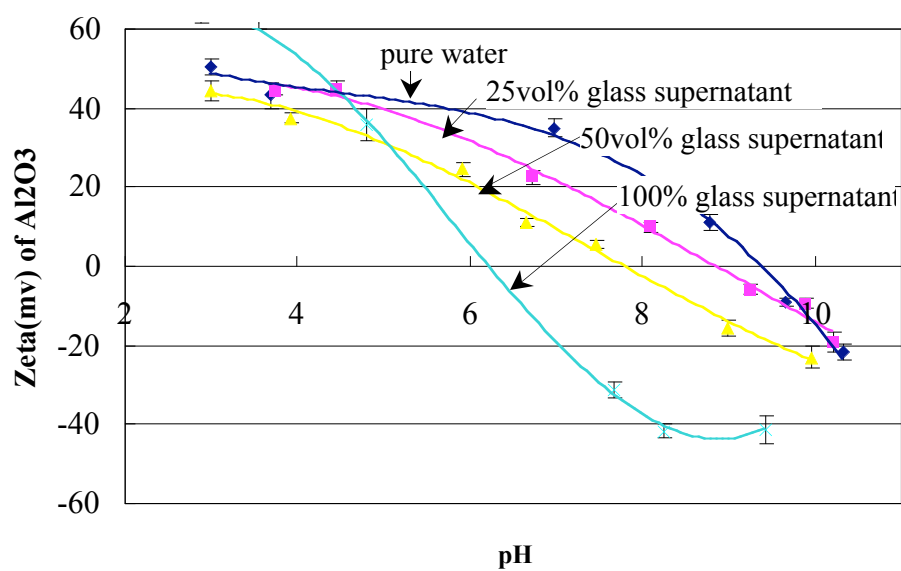


Figure 2 Zeta potential of 0.7 μ m Al₂O₃ (AA-07) particle in different concentration of glass supernatant

4. Conclusion

Soluble alumina species in alumina slurries were found to coat glass particles (and substrates) surface; like-wise, soluble silica species coated alumina particles. The dissolved species were charged ions, which changed the surface charge density of the other powder that was confirmed by the change in the zeta potential – pH function in our experiments. The IEP was shifted toward the dissolved material, and it shifted more with increasing amounts of dissolved species.

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